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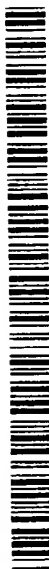


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(54) Title: DISINTEGRATING COMPONENT AND DETERGENT COMPOSITION CONTAINING IT

(57) Abstract: This invention relates to disintegrating components suitable for use in detergent compositions which will provide dissolution and/or dispensing benefits, preferably detergent compositions comprising cross-linked cellulose. The detergent compositions have good disintegration properties and therefore, good dispensing and/or residues properties. The invention also relates to detergent compositions or components thereof containing such disintegrating components. The detergent compositions of the invention may be in tablet form. Preferably cross-linked cellulose is combined with additional disintegrating agents, more preferably the disintegrating components comprise a wicking agent and a water-swellaable agent, preferably in an intimate mixture.

DISINTEGRATING COMPONENT AND DETERGENT COMPOSITION CONTAINING IT

Technical field

This invention relates to disintegrating components suitable for use in detergent or other compositions which will provide dissolution and/or dispensing benefits. The invention also relates to detergent or other compositions or components thereof containing such disintegrating components.

Background to the Invention

Over the last few decades, improvements in detergent compositions and in particular laundry and dish-washing detergent compositions, have generally been aimed at improving the cleaning performance of detergents. In more recent years, the focus has been on developing high density detergent products.

As detergent cleaning performance has improved and product density has tended to increase, it has now been found that one of the main complaints of the users of detergent products is that they do not always dispense or dissolve satisfactorily. This can be seen by residues of detergent product remaining in the dispenser drawer of a washing machine when a washing cycle has completed, and/or by residues of detergent product remaining on fabrics after the wash. The residues may be either gel residues (generally causing the residues found in the dispenser drawer) or in the form of powdered residues. Dispensing and dissolving problems are exacerbated by the tendency for increased product densities, especially in cooler water wash conditions and/or when limited amounts of water are used in the washing process, for example in the initial phase of the washing process where relatively small amounts of water are contacted with the detergent product. Poor dispensing results in an incomplete delivery of the detergent composition into the washing process and therefore, reduced cleaning performance.

In addition, it is desirable to produce detergent products in the form of a tablet for ease of use and convenience for the consumer. However, this further exacerbates any dispensing problems.

The tablet art discusses at length the problems and balance needed to produce detergent tablets which have sufficient strength and will still dispense. There are many disclosures of disintegrants for use in tablets. For example, in EP-A-466484, disintegrants and their mechanisms are discussed and it is stated that physical disintegrants which act by swelling are preferred. Examples include cross-linked polyvinyl pyrrolidone, montmorillonite or Bentonite clay, sodium carboxymethyl cellulose and acrylate/maleic anhydride copolymer. US4642197 discloses the use of more than one disintegrant such as a mixture of cross-linked polyvinylpyrrolidone and/or cellulose ethers and/or swellable magnesium aluminium silicate. However, detergent tablets preferably disintegrate very quickly or tablet fragments will be entrapped in either the dispenser, or in "dead areas" in the machine such as the area between the drum and the porthole in front loading automatic machines, or in the folds, creases and pockets of garments where the detergent is a laundry detergent. There is still therefore, a need for improved dispensing of detergent products and in particular for improved dispensing of detergent tablets. The inventors of the present invention have now found that particular cellulose compounds, and that a particular combination of components used together, are highly effective disintegrants.

Summary of the invention

In accordance with the present invention, there is now provided a detergent composition or component thereof comprising a cross-linked cellulose, preferably in an amount of from 0.1-25 wt%,

In accordance with a further aspect of the present invention, there is also provided a detergent composition comprising a combination of the cross-linked cellulose disintegrant with an additional water-swellaable disintegrant.

In accordance with the present invention, there is further now provided a disintegrating component for use in a detergent composition comprising a wicking agent and a water-swellaable polymer optionally in an intimate mixture.

In accordance with further aspects of the present invention, there is also provided a detergent composition comprising such a disintegrating component and a method for making a preferred disintegrating component.

Detailed description of the invention

The Wicking Agent, Including The Cross-Linked Cellulose

The wicking agent comprises a compound or mixture of compounds which enables fast water penetration into the detergent composition containing the disintegrating component, when the detergent composition is contacted with water in the wash. The wicking agent is generally substantially water-insoluble in cold water at 15°C. Preferably the wicking agent has a lower density than the density of the composition as a whole in which it is incorporated. The density of the wicking agent may be at least 10%, more preferably at least 20% (based on the density of the detergent composition as a whole) lower than the density of the composition as a whole in which it is incorporated. Preferably also, the wicking agent has low compressibility and maintains porosity under processing conditions, particularly compaction.

Suitable wicking agents are generally cellulose-based. The cellulose-based compounds may optionally be microcrystalline or mechanically ground and processed cellulose such as Arbocel™.

The wicking agent may be in the form of a powder, which may be obtained by mechanical grinding, a microcrystalline powder or it may be in the form of a granule e.g. an agglomerate of fine particle size wicking agent, or as a fibre, or mixtures thereof. Particularly preferred wicking agents are fibrous, for example, those having a length to diameter ratio of at least 3:1, preferably at least 5:1 or even at least 10:1. Suitable fibres include those having a length of at least 0.1mm, or at least 0.2mm, or even at least 0.4mm. Particularly preferred wicking agents are cross-linked.

The cross-linked celluloses for use in the detergent compositions of the present invention have been found to provide surprisingly effective disintegration of detergent compositions in which they are incorporated. It is believed that this is

because they resist detergent processing conditions and enable retention of a relatively high degree of porosity in the detergent matrix. They also provide hydrophilic structures which rapidly transport water molecules into the detergent composition. The cellulose is generally substantially water-insoluble in cold water at 15°C. The cellulose may have a lower density than the density of the composition as a whole in which it is incorporated. The density of the cross-linked cellulose may be at least 10%, more preferably at least 20% (based on the density of the detergent composition as a whole) lower than the density of the composition or component as a whole in which it is incorporated. Preferably also, the cross-linked cellulose has low compressibility and maintains porosity under processing conditions, particularly compaction.

The cross-linked cellulose may be in the form of a powder which may be microcrystalline, a fibre, or a granule. A powder may be obtained by mechanical grinding. A granule may be for example an extrudate or an agglomerate comprising fine particle size and/or fibrous cellulose or mixtures thereof. Particularly preferred cross-linked cellulose is fibrous, for example, fibres having a length to diameter ratio of at least 3:1, preferably at least 5:1 or even at least 10:1. Suitable fibres include those having an average length of 0.1mm, or 0.2mm, or even 0.4mm. Particularly preferred wicking agents are cross-linked.

Particularly preferred wicking agents are cross-linked cellulose fibres as described in US 5 137 537, US 5 183 707, US 5 190 563, US 5 562 740, US 5 549 791, US 5 549 863, US 5 709 774 or US 5 716 703. These particularly preferred cross-linked celluloses are in a substantially individualized form i.e. the cellulosic fibres have primarily intrafibre chemical cross-link bonds. That is, the cross-link bonds are primarily between cellulose molecules of a single fibre rather than between cellulose molecules of separate fibres. Processes for making such cross-linked fibres may be either dry cross-linking processes such as is described in US 3 224 926, or aqueous solution, as described in US 3 241 553 or non-aqueous solution cross-linking, as described in US 4 035 147.

Preferred cellulose is cross-linked with dialdehydes (as described in US 4 689 118 or US 4 822 453), epichlorohydrin, formaldehyde and more preferably by carboxylic acids (for example as described in US 5 137 537). The most preferred cellulose is cross-linked with citric acid. The cross-linked cellulose is preferably fluff-dried and is generally incorporated into a detergent composition or component thereof in amounts greater than 0.2 wt% or even greater than 0.5 wt%. Generally cross-linked cellulose will be incorporated in amounts below 10 wt% of a detergent composition, preferably below 7 wt%.

In a preferred aspect of the invention the cross-linked cellulose is used in combination with a water-swellaable agent. It is particularly preferred that it should be pre-mixed with the water-swellaable agent prior to addition to other detergent components.

The Water-Swellaable Agent

The water-swellaable agent may be any compound or mixture of compounds which swells in contact with water, for example to form a gel. The water-swellaable agent may be inorganic such as clays or water-swellaable salts, or organic such as polymeric materials. Preferably, the water-swellaable agent comprises a water-swellaable polymer. It may comprise a polyelectrolyte polymer such as poly(meth)acrylates or carboxymethylcellulose, copolymers or derivatives thereof such as polyacrylate esters, polymethacrylate esters, acrylate maleate copolymers or mixtures thereof. Polyvinyl pyrrolidones and their copolymers and derivatives are also suitable. The water-swellaable polymer may comprise polysaccharide polymers, such as guar, alginates, starches, carboxymethyl starches, optionally colloidal microcrystalline cellulose, their copolymers or derivatives or mixtures thereof. Mixtures of polyelectrolyte and polysaccharide polymers are also suitable. The polymers may be in the acid or salt form with varying degrees of charge/neutralisation and of varying molecular weight and have varying degrees of and distribution of substituents, as long as they are swellaable. The polymers are optionally cross-linked. Carboxymethylcellulose and its derivatives are particularly preferred, especially those having a degree of substitution of from 0.2 to 0.7, preferably from 0.4 to 0.6 and a

molecular weight of from 250,000 to 1,000,000, preferably from 250,000 to 700,000 measured for example by GPC using styrene as a standard.

In the disintegrating component, the wicking agent and water-swellaable agent are preferably present in weight ratios of less than 2:1, preferably less than 1:1. The weight ratio is generally no less than 1:20, preferably no less than 1:10. The water-swellaable agent may be used in combination with the cross-linked cellulose preferably in weight ratios of less than 2:1, preferably less than 1:1. The weight ratio is generally no less than 1:20, preferably no less than 1:10.

Where the disintegrating component is formed as an intimate mixture of the wicking agent, preferably the cross-linked cellulose, and water-swellaable agent in a pre-mix for incorporation into a composition such as a detergent composition, the pre-mix may be in the form of a detergent component, for example in the form of a particle. The pre-mix preferably comprises more than 50 wt%, preferably more than 75 wt% or even up to 90 wt% of wicking agent and water-swellaable polymer and less than 50 wt %, preferably less than 25 wt% or even less than 10 wt% other ingredients optionally comprising a binder. Other ingredients suitable for incorporation into the pre-mix are dependent on the final application of the disintegrating component. When the disintegrating component is for incorporation into a detergent composition, conventional detergent ingredients are suitable as the other ingredients. The binder may be present in relatively high levels, for example up to 50 wt% of the pre-mix or detergent component, however the binder is generally present in amounts no greater than 25 wt% of the pre-mix, or even amounts below 20 wt% or below 10 wt%.

The disintegrating component may be added to a composition for disintegrating such as a detergent composition, preferably a detergent tablet, preferably as a pre-formed component or may be added as the individual components of the disintegrating component directly and individually into detergent processing steps. The respective components or a pre-formed particle or other detergent component may be added as a dry-add, or into a crutcher mix for forming a spray dried detergent product or may be incorporated into an agglomeration step.

The cross-linked cellulose and optional water-swellaable agent may be incorporated into a detergent composition (preferably a detergent tablet), individually, or where used in combination, preferably as a pre-mix comprising the water-swellaable agent and cross-linked cellulose, into detergent processing steps. The cross-linked cellulose and optional water-swellaable agent or pre-mix may be added as a dry-add, or into a crutcher mix for forming a spray dried detergent product or may be incorporated into a granulation process such as an agglomeration or extrusion step. When the detergent composition is used to produce a tablet, the individual components or, preferably the pre-mix is added at any stage prior to tableting.

In a final detergent composition, the disintegrating component is generally present in amounts no greater than 20 wt%, preferably no greater than 10 wt% based on the finished detergent composition as a whole. The amount of water-swellaable agent is generally from at least 1.5 wt% based on the composition for disintegrating, as a whole, generally being no greater than 10 wt % of a finished composition, preferably from 1.5-7 wt%. The disintegrating agents of the invention are particularly useful in detergent compositions, especially detergent particles or tablets, or in pesticidal, herbicidal, sanitizing or pharmaceutical compositions.

The cross-linked cellulose, optionally as a pre-mix in combination with a water-swellaable agent, may be in the form of a detergent component, for example in the form of a particle. The detergent component will generally comprise no more than 95 wt% of water-swellaable agent and/or other detergent ingredients and/or binders. Preferably such a detergent component comprises no more than 50 wt%, of water-swellaable agent and/or other detergent ingredients and/or binders, most preferably no more than 45 wt%. The binder may be present in relatively high levels, for example up to 50 wt% of the detergent component, however the binder is generally present in amounts no greater than 25 wt% , or even amounts below 20 wt% or below 10 wt%.

The disintegrating component may be added to a composition for disintegrating such as a detergent composition, preferably a detergent tablet, preferably as a pre-formed

component or may be added as the individual components of the disintegrating component directly and individually into detergent processing steps. The respective components or a pre-formed particle or other detergent component may be added as a dry-add, or into a crutcher mix for forming a spray dried detergent product or may be incorporated into an agglomeration step.

The amount of water-swellaable agent in the detergent composition is generally from 1.5 wt% based on the composition for disintegrating, as a whole, generally being no greater than 10 wt % of a finished composition, preferably from 1.5-7 wt%.

Intimate Mixture

Preferably the wicking agent and water-swellaable agent of the disintegrating component are added to a composition for improving disintegration/dissolution in the form of an intimate mixture of the two components optionally with additional components and/or binder as described above. By intimate mixture is meant that the at least two components are mixed together to form a pre-mix which is a substantially homogeneous mixture. Preferably the detergent composition comprises cross-linked cellulose in combination with a water-swellaable agent in an intimate mixture of the two components optionally with additional components and/or binder as described above.

This may be achieved by dry mixing solid wicking agent, preferably cross-linked cellulose, and solid water-swellaable agent with an optional binder. The pre-mix may be in the form of a particle and this can be achieved for example by granulation, such as by agglomeration, extrusion or dry compaction. However, it has been found that particularly effective results are achieved if the water-swellaable agent is present as a coating on the wicking agent, preferably cross-linked cellulose. This is particularly beneficial where the wicking agent, preferably cross-linked cellulose, is fibrous.

The wicking agent, preferably cross-linked cellulose, and water-swellaable agent may be mixed together, optionally with a binder and then ground to enhance mixing and reduce particle size. This is particularly useful if the wicking agent is provided as

relatively large particles or fibres. Grinding as a mixture enables more effective reduction of the length of the fibres or particle size in combination with effective mixing.

Providing a coating of the water-swellaable agent on the wicking agent, preferably cross-linked cellulose, may be achieved in any convenient way, for example by mixing the cross-linked cellulose and water-swellaable agent with a solvent for the water-swellaable agent, in any order of addition, such that a gel or solution is formed or a slurry comprising partially swollen water-swellaable agent. Preferably mixing is continued until a substantially homogeneous mixture is obtained. The mixture of wicking agent, preferably cross-linked cellulose, and water-swellaable agent is then recovered by separating out from the solvent by any conventional technique, such as by evaporating off the solvent or by addition of a non-solvent for the water-swellaable agent to form a precipitate of the mixture, such mixture is then separated from the solvent by any conventional technique such as by subsequent filtration or decanting off the solvent.

The separated solid is preferably recovered directly in an appropriate particle size for direct addition into a detergent composition processing stage. Alternatively, the solid mixture may be recovered having a particle size greater than that required for final use and if so, may be treated to reduce the particle size, for example by grinding. Should the product mixture be obtained as fine particulates these may be mixed with optional binder or additional detergent components and formed into a granule as described above, for example, by agglomeration to produce very fine particulates adhered to one another in the form of a disintegrating component which is a granule.

In a preferred process, in a first step, the water-swellaable agent preferably polymer, and solvent, preferably water, are mixed together to form a gel, solution or slurry, and the wicking agent, preferably cross-linked cellulose, is subsequently added to the gel, solution or slurry. This process is particularly advantageous as it can be used as the final stages in the industrial manufacture of water-swellaable agents, particularly polymers. Where the later stages of preparation of a water-swellaable agent require the

recovery of the polymer from a solvent, the wicking agent, preferably cross-linked cellulose, may be added directly to the mixture in solvent prior to recovery. This may be particularly useful, for example, where the water-swellaable agent comprises a polymer. In particular this method can be applied where the polymer comprises CMC as in the manufacture of CMC, a very viscous slurry of CMC is obtained in water and then the wicking agent, preferably fibrous wicking agent (such as cross-linked cellulose), may be added directly to the slurry prior to the recovery of the CMC. The mixture of wicking agent, preferably cross-linked cellulose, and water-swellaable polymer may then be recovered as described above.

It has been found that the particle size of the disintegrating component, preferably a particle containing the cross-linked cellulose, may be selected to give particularly beneficial disintegrating properties in use in a detergent composition. Disintegrating components or the respective materials in a disintegrating component preferably have a particle size of at least 100 μ m, preferably at least 150 μ m. Preferred disintegrating components have a particle size of no greater than 2000 μ m, most preferably below 1700 μ m. In practice, the particles obtained may have a size distribution. Therefore, the particle size is preferably such that at least 80 wt%, preferably at least 90 wt% and most preferably at least 95 wt% of the components of the disintegrating component or a particulate disintegrating component is at least 100 μ m, more preferably at least 150 μ m. Preferably at least 80 wt%, preferably at least 90 wt% and most preferably at least 95 wt% disintegrating agent is below 2000 μ m, most preferably below 1700 μ m, or even below 1500 μ m, to obtain the maximum disintegrating benefits.

The Binder

The optional binder which may be incorporated as part of the disintegrating component may be any conventional binder. Water, organic acids, hydratable salts or alcohols are all suitable. Water or alcohols such as glycerol are particularly preferred.

The optional binder which may be incorporated into the pre-mix or granule comprising cross-linked cellulose optionally in combination with water-swellaable

agent may be for example water, organic acids, hydratable salts, alcohols or mixtures thereof. Water or alcohols such as glycerol are particularly preferred.

Optional Additional Components

The disintegrating component of the invention may contain additional ingredients which depend on the final use of the component. When the disintegrating component is for use in a detergent composition, the additional ingredients may comprise optional additional detergent components.

The detergent ingredients mentioned below as suitable ingredients for the detergent composition are all suitable as the optional additional detergent components which may be present in the disintegrating component. It may be particularly preferred to incorporate a surfactant, such as an anionic, nonionic, zwitterionic or cationic surfactant as this may increase the wicking/swelling action of the respective components.

It may be preferred to pre-mix the cross-linked cellulose with a surfactant, such as an anionic, nonionic, zwitterionic or cationic surfactant, prior to incorporation into a detergent composition, as this may increase the effectiveness of the cross-linked cellulose.

Detergent Composition

In accordance with a further aspect of the present invention there is provided a detergent composition comprising a disintegrating component as described above.

The disintegrating component is particularly useful in detergent compositions comprising high levels of surfactant, for example at least 20 % by weight, preferably at least 25% by weight or even at least 40 or 45% by weight based on the detergent composition. In such high surfactant formulations, dispensing and gelling of the detergent composition are a particular problem and the benefits of the invention may be most significant.

Form of the Composition

The detergent compositions of the invention may take a variety of physical forms but are preferably solid forms such as tablet, flake, pastille and bar, and preferably granular or tablet forms. The particulate processing composition may be made by a variety of methods, including dry-mixing, agglomerating, compaction, or spray-drying of the various compounds comprised in the detergent composition, or mixtures of these techniques.

The compositions in accordance with the present invention can also be used in or in combination with bleach additive compositions, for example comprising chlorine or oxygen bleach.

Detergent compositions herein, in particular laundry detergents, preferably have a bulk density of from 450 g/litre to 1500 g/litre, or preferably from 500 g/litre or even 600g/litre or 650g/litre to 2000g/litre or more preferably to 1500g/litre.

Where the composition is provided as a tablet, the tablets are generally prepared by compaction of a particulate starting material. Any conventional tableting process and apparatus may be used. The optimum compaction pressure will depend to some extent on the starting composition; for example a formulation containing a high proportion of organic ingredients (for example, surfactants) and a relatively low proportion of inorganic salts generally requires a compaction pressure lower than that required for a formulation containing a lower proportion of organic ingredients and a higher proportion of inorganic salts. A dry-mixed formulation generally requires a higher pressure than a spray-dried powder. However, as a result of the present invention, higher compaction pressures may be used so that increased tablet hardness can be achieved without adversely affecting disintegration times, compared to products which do not incorporate the disintegrating component of the invention. Thus, increased tablet hardness and/or increased disintegration times can be achieved.

The detergent composition of the invention is preferably a complete heavy-duty laundry composition. Although one tablet may contain sufficient detergent components to provide cleaning for an average wash load, the tablets formed may be

smaller such that the consumer may choose the number of detergent tablets required according to the size and nature of the wash load. For example, tablet sizes may be chosen such that two tablets are sufficient for an average wash load, with one additional tablet to be used for particularly heavily soiled laundry. For smaller washes, a smaller tablet may be preferred. The tablet will generally be from 10-160 g and may be any suitable shape. The tablet may be homogenous or may consist of more than one discrete region. For example, the tablet may comprise two or more layers of different detergent composition or a core region may be surrounded by outer regions of different detergent compositions.

The tablet may be coated or uncoated. Suitable coating materials are described for example in EP-A-2293, GB-A-0989683 and EP-A-716144.

Detergent Ingredients

The composition or component thereof according to the present invention is preferably a detergent composition or component thereof which will comprise additional detergent ingredients. The precise nature of these additional ingredients, and levels of incorporation thereof will depend on the application of the component or compositions and the physical form of the components and the compositions.

The detergent compositions of the invention preferably contain one or more additional detergent components selected from bleaches, bleach catalysts, alkalinity systems, additional builders, organic polymeric compounds, enzymes, suds suppressors, lime soap, dispersants, soil suspension and anti-redeposition agents soil releasing agents, perfumes, brighteners, photobleaching agents and additional corrosion inhibitors.

Surfactant

The compositions of the invention contain one or more surfactants. The surfactant may comprise any surfactant known in the art, selected from anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants such as those discussed below and mixtures thereof.

Anionic Surfactant

The compositions in accordance with the present invention preferably comprise an anionic surfactant. Any anionic surfactant useful for deterative purposes can be present in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate and sulfonate surfactants are preferred. Highly preferred are surfactants systems comprising a sulfonate, preferably a linear or branched alkyl benzene sulfonate, as described herein, preferably combined with a cationic surfactant as described herein.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12} - C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6 - C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Preferably the detergent composition comprises at least one anionic surfactant, preferably an anionic sulphonate surfactant, preferably an alkyl sulphonate surfactant, as described herein. More preferably, the anionic surfactant comprises from 50% to 100% or even from 60% to 100% or even from 75% to 100% by weight of the surfactant content of the detergent composition.

Anionic Sulphonate Surfactant

Highly preferred surfactants are anionic sulphonate surfactants. Particularly suitable for use herein include the salts of C_5 - C_{20} linear or branched alkylbenzene sulphonates, but also may be used alkyl ester sulphonates, C_6 - C_{22} primary or secondary alkane sulphonates, C_6 - C_{24} olefin sulphonates, sulphonated

polycarboxylic acids, alkyl glycerol sulphonates, fatty acyl glycerol sulphonates, fatty oleyl glycerol sulphonates, and any mixtures thereof. Most preferred are C_9 - C_{14} linear alkyl benzene sulphonates.

Anionic Sulfate Surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5 - C_{17} acyl-N-(C_1 - C_4 alkyl) and -N-(C_1 - C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_{10} - C_{18} alkyl sulfates, more preferably the C_{11} - C_{15} branched chain alkyl sulfates and the C_{12} - C_{14} linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10} - C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11} - C_{18} , most preferably C_{11} - C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and/ or sulfonate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic Carboxylate Surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_2O)_xCH_2COO^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Soaps may also be included as suds suppressors and if so, is generally present in low levels up to 5 wt % as finely divided particulates or flakes.

Alkali Metal Sarcosinate Surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R-CON(R^1)CH_2COOM$, wherein R is a C_5 - C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1 - C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Alkoxyated Nonionic Surfactant

Any alkoxyated nonionic surfactant is suitable for use herein. The ethoxylated and propoxylated nonionic surfactants are preferred. Particularly preferred alkoxyated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty

alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic Alkoxylated Alcohol Surfactant

Nonionic surfactant may be present in the detergent compositions of the invention. It may be preferred that the level of ethoxylated nonionic surfactants in the intimate mixture are below 10% by weight of the mixture, preferably even 5% by weight.

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic Polyhydroxy Fatty Acid Amide Surfactant

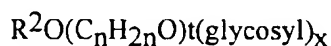
Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight-chain C_5 - C_{19} alkyl or alkenyl, more preferably straight-chain C_9 - C_{17} alkyl or alkenyl, most preferably straight-chain C_{11} - C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glyceryl.

Nonionic Fatty Acid Amide Surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6\text{CON}(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic Alkylpolysaccharide Surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units. Preferred alkylpolyglycosides have the formula:

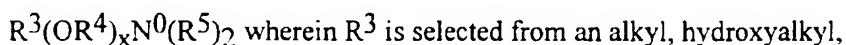


wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric Surfactant

Suitable amphoteric surfactants for use in the detergent compositions of the invention herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula



acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide. An

example of a suitable alkyl aphodicarboxylic acid is Miranol™ C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic Surfactant

Zwitterionic surfactants may also be incorporated into the detergent compositions of the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, each R¹ is typically C₁-C₃ alkyl, and R² is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂₋₁₈ dimethyl-ammonio hexanoate and the C₁₀₋₁₈ acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

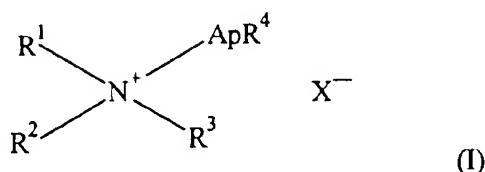
Cationic Surfactants

Suitable cationic surfactants for incorporation into the detergent composition of the invention include the quaternary ammonium surfactants. Preferably the quaternary ammonium surfactant is a mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Preferred are also the mono-alkoxylated and bis-alkoxylated amine surfactants.

Another suitable group of cationic surfactants which can be used in the detergent composition of the invention are cationic ester surfactants such as those disclosed in US Patents Nos. 4228042, 4239660 and 4260529.

Cationic mono-alkoxylated amine surfactants

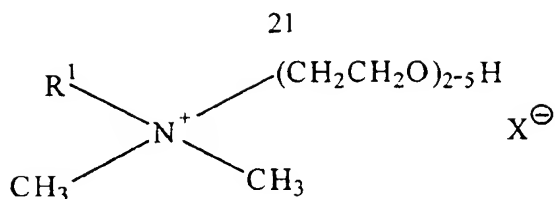
Highly preferred herein are cationic mono-alkoxylated amine surfactant preferably of the general formula I:



wherein R^1 is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 14 carbon atoms; R^2 and R^3 are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl, most preferably both R^2 and R^3 are methyl groups; R^4 is selected from hydrogen (preferred), methyl and ethyl; X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is a alkoxy group, especially a ethoxy, propoxy or butoxy group; and p is from 0 to about 30, preferably 2 to about 15, most preferably 2 to about 8.

Preferably the ApR^4 group in formula I has $p=1$ and is a hydroxyalkyl group, having no greater than 6 carbon atoms whereby the —OH group is separated from the quaternary ammonium nitrogen atom by no more than 3 carbon atoms. Particularly preferred ApR^4 groups are $\text{—CH}_2\text{CH}_2\text{OH}$, $\text{—CH}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{—CH}_2\text{CH}(\text{CH}_3)\text{OH}$ and $\text{—CH}(\text{CH}_3)\text{CH}_2\text{OH}$, with $\text{—CH}_2\text{CH}_2\text{OH}$ being particularly preferred. Preferred R^1 groups are linear alkyl groups. Linear R^1 groups having from 8 to 14 carbon atoms are preferred.

Other highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula



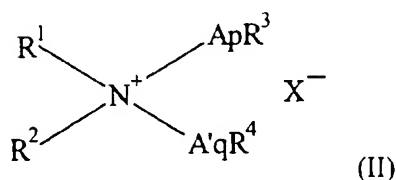
wherein R^1 is C_{10} - C_{18} hydrocarbyl and mixtures thereof, especially C_{10} - C_{14} alkyl, preferably C_{10} and C_{12} alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

As noted, compounds of the foregoing type include those wherein the ethoxy $(\text{CH}_2\text{CH}_2\text{O})$ units (EO) are replaced by butoxy, isopropoxy $[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]$ and $[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]$ units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

The levels of the cationic mono-alkoxylated amine surfactants used in detergent compositions of the invention is preferably from 0.1% to 20%, more preferably from 0.2% to 7%, most preferably from 0.3% to 3.0% by weight of the composition.

Cationic bis-alkoxylated amine surfactant

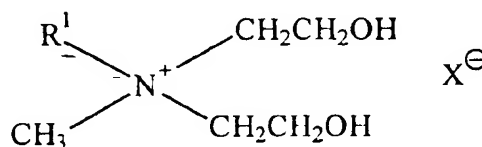
Suitable cationic bis-alkoxylated amine surfactants preferably have the general formula II:



wherein R^1 is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R^4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A'

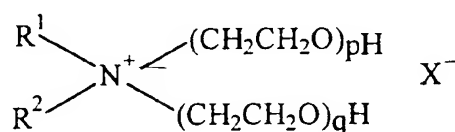
can vary independently and are each selected from C₁-C₄ alkoxy, especially ethoxy, (i.e., -CH₂CH₂O-), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



wherein R¹ is C₁₀-C₁₈ hydrocarbyl and mixtures thereof, preferably C₁₀, C₁₂, C₁₄ alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R¹ is derived from (coconut) C₁₂-C₁₄ alkyl fraction fatty acids, R² is methyl and ApR³ and A'qR⁴ are each monoethoxy.

Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



wherein R¹ is C₁₀-C₁₈ hydrocarbyl, preferably C₁₀-C₁₄ alkyl, independently p is 1 to about 3 and q is 1 to about 3, R² is C₁-C₃ alkyl, preferably methyl, and X is an anion, especially chloride or bromide.

Other compounds of the foregoing type include those wherein the ethoxy (CH₂CH₂O) units (EO) are replaced by butoxy (Bu) isopropoxy [CH(CH₃)CH₂O] and [CH₂CH(CH₃O)] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

Perhydrate Bleaches

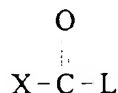
A preferred additional component of the detergent compositions of the invention is a perhydrate bleach, such as metal perborates, metal percarbonates, particularly the sodium salts. Perborate can be mono or tetra hydrated. Sodium percarbonate has the formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Potassium peroxymonopersulfate, sodium per is another optional inorganic perhydrate salt of use in the detergent compositions herein.

Organic Peroxyacid Bleaching System

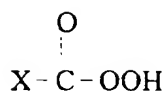
The detergent composition of the invention preferably comprise an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches, such as the perborate bleach of the claimed invention. In an alternative execution, a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Peroxyacid Bleach Precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

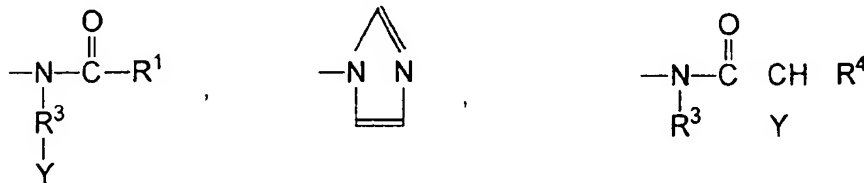
Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes.

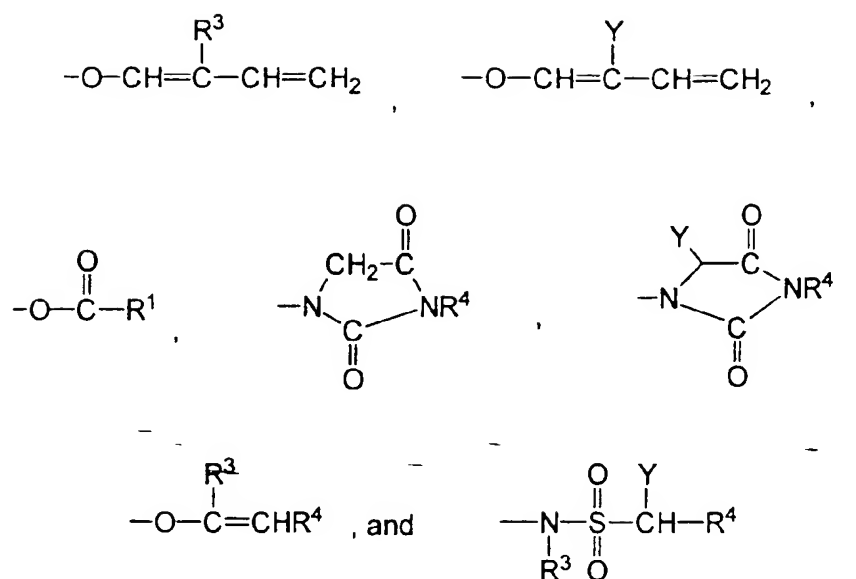
Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving Groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:





and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups. The preferred solubilizing groups are $-\text{SO}_3^- \text{M}^+$, $-\text{CO}_2^- \text{M}^+$, $-\text{SO}_4^- \text{M}^+$, $-\text{N}^+(\text{R}^3)_4 \text{X}^-$ and $\text{O}=\text{N}(\text{R}^3)_3$ and most preferably $-\text{SO}_3^- \text{M}^+$ and $-\text{CO}_2^- \text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Alkyl Percarboxylic Acid Bleach Precursors

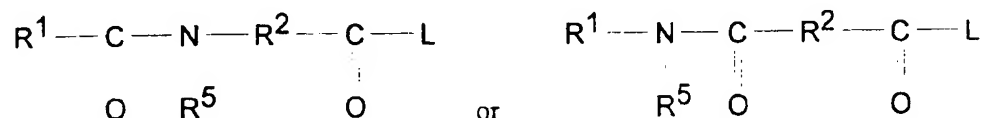
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred. The TAED is preferably not present in the agglomerated particle of the present invention, but preferably present in the detergent composition, comprising the particle.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide Substituted Alkyl Peroxyacid Precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R¹ is an alkyl group with from 1 to 14 carbon atoms, R² is an alkylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic Acid Precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-

benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic Peroxyacid Precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

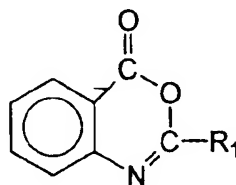
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332. Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the

trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin Organic Peroxyacid Precursors

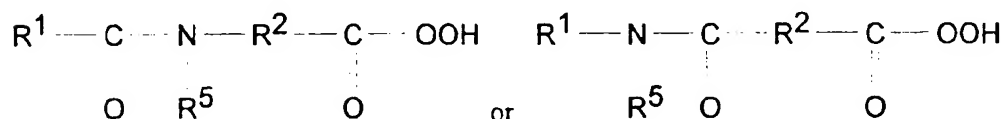
Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:



wherein R_1 is H, alkyl, alkaryl, aryl, or arylalkyl.

Preformed Organic Peroxyacid

The detergent composition may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition. A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Bleach Catalyst

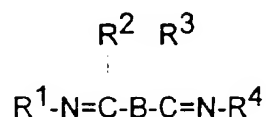
The composition can contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})(\text{OCH}_3)_3(\text{PF}_6)$.

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein R^1 , R^2 , R^3 , and R^4 can each be selected from H, substituted alkyl and aryl groups such that each $\text{R}^1-\text{N}=\text{C}-\text{R}^2$ and $\text{R}^3-\text{C}=\text{N}-\text{R}^4$ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR^5R^6 , NR^7 and $\text{C}=\text{O}$, wherein R^5 , R^6 , and R^7 can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe, -bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include $\text{Co}(2,2'\text{-bispyridylamine})\text{Cl}_2$, $\text{Di}(\text{isothiocyanato})\text{bispyridylamine-cobalt (II)}$, $\text{tris}(\text{dipyridylamine-cobalt(II)})\text{perchlorate}$, $\text{Co}(2,2'\text{-bispyridylamine})_2\text{O}_2\text{ClO}_4$, $\text{Bis}(2,2'\text{-bispyridylamine})\text{copper(II) perchlorate}$, $\text{tris}(\text{di-2-pyridylamine})\text{iron(II) perchlorate}$, and mixtures thereof.

Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4)^+$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$. Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts),

European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

The bleach catalyst is typically used in a catalytically effective amount in the compositions and processes herein. By "catalytically effective amount" is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance bleaching and removal of the stain or stains of interest from the target substrate. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some users elect to use very hot water; others use warm or even cold water in laundering operations. Of course, the catalytic performance of the bleach catalyst will be affected by such considerations, and the levels of bleach catalyst used in fully-formulated detergent and bleach compositions can be appropriately adjusted. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 1 ppm to about 200 ppm of the catalyst species in the wash liquor. To illustrate this point further, on the order of 3 micromolar manganese catalyst is effective at 40°C, pH 10 under European conditions using perborate and a bleach precursor. An increase in concentration of 3-5 fold may be required under U.S. conditions to achieve the same results.

Builders

Water-Soluble Builders

The detergent compositions according to the present invention preferably contain a water-soluble builder compound, typically present in detergent compositions at a

level of from 1% to 80% by weight, preferably from 10% to 60% by weight, most preferably from 15% to 40% by weight of the composition.

The detergent compositions of the invention may comprise phosphate-containing builder material, preferably comprises tetrasodium pyrophosphate or even more preferably anhydrous or partially hydrated sodium tripolyphosphate, present at a level of from 0.5% to 60%, more preferably from 5% to 50%, more preferably from 8% to 40. It may be preferred that the compositions are free of phosphate-containing builder material.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates or their acids containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447. The most preferred polycarboxylic acid containing three carboxy groups

is citric acid, preferably present at a level of from 0.1% to 15%, more preferably from 0.5% to 8% by weight of the composition.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

It may be preferred that the polymeric or oligomeric polycarboxylates are present at levels of less than 5%, preferably less than 3% or even less than 2% or even 0% by weight of the compositions.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

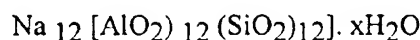
Water-soluble builders may also prove to be useful binding agents.

Insoluble Builder Compound

The compositions according to the present invention may contain an insoluble builder compound, but preferably in relatively low amounts at a level of from 0% to 25% by weight, most preferably from 0% to 15% weight of the composition, or even 0% to 10% by weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates. Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula:



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Another preferred aluminosilicate zeolite is zeolite MAP builder. Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

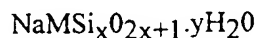
Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a d₅₀ value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

The d_{50} value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer. Other methods of establishing d_{50} values are disclosed in EP 384070A.

Crystalline layered silicate

Crystalline layered silicate builder may also be incorporated in the detergent compositions of the invention. These have the general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. M is preferably H, K or Na or mixtures thereof, preferably Na. The most preferred material is α - $\text{Na}_2\text{Si}_2\text{O}_5$, β - $\text{Na}_2\text{Si}_2\text{O}_5$ or δ - $\text{Na}_2\text{Si}_2\text{O}_5$, or mixtures thereof, preferably being at least 75% $\text{Na}_2\text{Si}_2\text{O}_5$, for example available from Clariant as NaSKS-6.

It may be preferred that crystalline layered silicate is present as a coarse material having a weight average particle size above 150 microns, as measurable by sieving on Tyler sieves, or fine material of weight average particle size below 20 microns, Malvern Instruments SB.OC light scattering equipment.

Heavy metal ion sequestrant

Heavy metal ion sequestrants are also useful additional ingredients in the detergent compositions of the invention. By heavy metal ion sequestrant is meant components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferably they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 10%, preferably from 0.1% to 5%, more preferably from 0.25% to 7.5% and most preferably from 0.3% to 2% by weight of the compositions.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy diphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate, 1,1 hydroxyethane diphosphonic acid and 1,1 hydroxyethane dimethylene phosphonic acid.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic

acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.

Especially preferred are diethylenetriamine pentacetic acid, ethylenediamine-N,N'-disuccinic acid (EDDS) and 1,1 hydroxyethane diphosphonic acid or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Enzyme

Another preferred ingredient useful herein is one or more additional enzymes. Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl, Duramyl and BAN by Novo Industries A/S. Highly preferred amylase enzymes may be those described in PCT/US 9703635, and in WO95/26397 and WO96/23873.

Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomonas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Additional Organic Polymeric Compound

Organic polymeric compounds are optional additional components of the compositions of the present invention.

By organic polymeric compound is meant any polymeric organic compound commonly used as anti-redeposition or soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein, including quaternised ethoxylated (poly) amine clay-soil removal/ anti-redeposition agent in accord with the invention.

Additional organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.01% to 30%, preferably from 0.1% to 15%, most preferably from 0.5% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

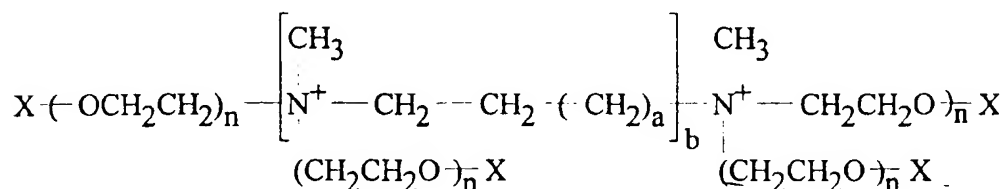
Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Highly preferred polymeric components herein are cotton and non-cotton soil release polymer according to U.S. Patent 4,968,451, Scheibel et al., and U.S. Patent 5,415,807, Gosselink et al., and in particular according to US application no.60/051517.

Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and diamines of the formula:



wherein X is a nonionic group selected from the group consisting of H, C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

Suds Suppressing System

The detergent compositions of the invention, when formulated for use in machine washing compositions, may comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.02% to 10%, most preferably from 0.05% to 3% by weight of the composition. Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alanol antifoam compounds. By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises: (a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination (i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and (ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound; wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight; (b) a

dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544; and (c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

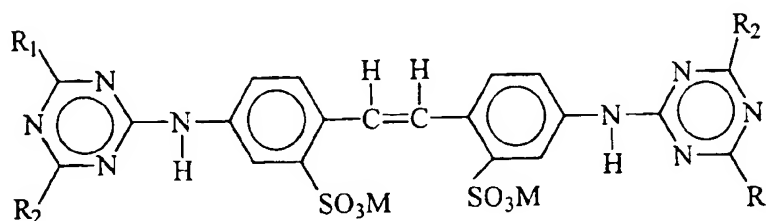
Other highly preferred suds suppressing systems comprise polydimethylsiloxane or mixtures of silicone, such as polydimethylsiloxane, aluminosilicate and polycarboxylic polymers, such as copolymers of laic and acrylic acid.

Polymeric Dye Transfer Inhibiting Agents

The compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents. The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers are optionally cross-linked polymers.

Optical Brightener

The compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners. Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morpholino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-CBS-X and Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morpholino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morpholino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species are

commercially marketed under the tradename Tinopal-DMS-X and Tinopal AMS-GX by Ciba Geigy Corporation.

Polymeric Soil Release Agent

Polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present compositions. If utilized, SRAs will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions. Preferred SRAs typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

Preferred SRAs include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely cross-linked overall structure.

Suitable SRAs include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by

transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRAs also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C₁-C₄ alkyl celluloses and C₄ hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRAs include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRAs with carboxylate terminal groups made by adding trimellitic anhydride to known SRAs to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the

isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRAs of the urethane-linked variety, see U.S. 4,201,824, Violland et al.;

Other Optional Ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, speckles, colours or dyes, filler salts, with sodium sulfate being a preferred filler salt. Also, minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides and dyes, such as those described in US Patent 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference), can be present.

Laundry Washing Method

Machine laundry methods for using laundry detergent compositions according to the present invention typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accordance with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

The composition may also be formulated such that it is suitable for disinfecting, sanitisation, hard-surface cleaning or hand washing or for pre-treatment or soaking of soiled and stained fabrics.

The invention will now be illustrated by way of examples.

Abbreviations used in the Examples

In the disintegrating components/detergent compositions, exemplified below, the abbreviated component identifications have the following meanings:

NYMCEL™	:	Carboxymethyl cellulose (degree of substitution 0.3) supplied by Metsa-Serla
CMF	:	Citric acid intra-cross-linked fibrous cellulose made by Wayerhauser
Arbocel™	:	Micronised cellulose supplied by Rettesmeyer
LAS	:	Sodium linear C ₁₁₋₁₃ alkyl benzene sulfonate
MES	:	α -sulpho methylester of C ₁₈ fatty acid
TAS	:	Sodium tallow alkyl sulfate
CxyAS	:	Sodium C _{1x} - C _{1y} alkyl sulfate
C46SAS	:	Sodium C ₁₄ - C ₁₆ secondary (2,3) alkyl sulfate
CxyEzS	:	Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide
CxyEz	:	C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
QAS	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄
QAS 1	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ - C ₁₁
SADS	:	Sodium C ₁₄ -C ₂₂ alkyl disulfate of formula 2-(R).C ₄ H ₇ -1,4-(SO ₄) ₂ where R = C ₁₀ -C ₁₈
SADE2S	:	Sodium C ₁₄ -C ₂₂ alkyl disulfate of formula 2-(R).C ₄ H ₇ -1,4-(SO ₄) ₂ where R = C ₁₀ -C ₁₈ , condensed with z moles of ethylene oxide
APA	:	C ₈ - C ₁₀ amido propyl dimethyl amine
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
STS	:	Sodium toluene sulphonate
CFAA	:	C ₁₂ -C ₁₄ (coco) alkyl N-methyl glucamide

TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
TPKFA	:	C ₁₆ -C ₁₈ topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
TSPP	:	Tetrasodium pyrophosphate
Zeolite A	:	Hydrated sodium aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ ·27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
NaSKS-6 (I)	:	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅ of Clariant
Citric acid	:	Anhydrous citric acid
Borate	:	Sodium borate
Carbonate	:	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate	:	Amorphous sodium silicate (SiO ₂ :Na ₂ O = 2.0:1)
Sulfate	:	Anhydrous sodium sulfate
Mg sulfate	:	Anhydrous magnesium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
MA/AA (1)	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	:	Sodium carboxymethyl cellulose
Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals

Protease	:	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
Protease I	:	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
Alcalase	:	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
Amylase II	:	Amylolytic enzyme, as disclosed in PCT/ US9703635
Lipase	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
Lipase (1)	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
Endolase	:	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Percarbonate	:	Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
DOBS	:	Decanoyl oxybenzene sulfonate in the form of the sodium salt
DPDA	:	Diperoxydodecanedioc acid

NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt
NACA-OBS	:	(6-nonamidocaproyl) oxybenzene sulfonate
LOBS	:	Dodecanoyloxybenzene sulfonate in the form of the sodium salt
DOBS	:	Decanoyloxybenzene sulfonate in the form of the sodium salt
DOBA	:	Decanoyl oxybenzoic acid
TAED	:	Tetraacetythylenediamine
DTPA	:	Diethylene triamine pentaacetic acid
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
Photoactivated	:	Sulfonated zinc phthlocyanine encapsulated in bleach (1) dextrin soluble polymer
Photoactivated	:	Sulfonated alumino phthlocyanine encapsulated in bleach (2) dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2,2'-disulfonate
HEDP	:	1,1-hydroxyethane diphosphonic acid
PEGx	:	Polyethylene glycol, with a molecular weight of x (typically 4,000)
PEO	:	Polyethylene oxide, with an average molecular weight of 50,000
TEPAE	:	Tetraethylenepentaamine ethoxylate
PVI	:	Polyvinyl imidosole, with an average molecular weight of 20,000
PVP	:	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000

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PVNO	:	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
QEA	:	bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ -(CH ₃) bis((C ₂ H ₅ O)-(C ₂ H ₄ O)) _n , wherein n = from 20 to 30
SRP 1	:	Anionically end capped poly esters
SRP 2	:	Diethoxylated poly-(1, 2 propylene terephthalate) short block polymer
PEI	:	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
Opacifier	:	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
Wax	:	Paraffin wax

Examples

Disintegrating components according to the present invention were prepared as follows.

Example 1: Preparation of 85% active Agglomerate (25% CMF with 75% Nymcel) + 15 wt % Glycerol

Finely ground curly cellulose CMF (3 g) is placed in the 1l pot of a Braun Combimax 700 food processor with Nymcel (9 g). Glycerol (2.2 g) is added dropwise as a binder and the mixture is stirred gently for 2 minutes before being sieved such that all retained agglomerate material has a diameter d<2 mm. This yields 14 g of agglomerate [85% (25% CMF with 75% Nymcel) + 15% Glycerol].

Example 2: Preparation of 66 wt % Agglomerate (25% CMF with 75% Nymcel) + 33 wt % stearic acid

A disintegrating component agglomerate was prepared as for example 1, but using 6 g of melted stearic acid instead of 2.2 g of glycerol.

Example 3: Preparation of 85 wt % Agglomerate (25% Arbocel with 75% Nymcel) + 15% Glycerol

A disintegrating component agglomerate was prepared as in example 1 but using 3 g of Arbocel instead of 3 g of curly cellulose CMF

Example 4: Preparation of 25 wt % CMF coated with 75 wt % Nymcel

Curly cellulose CMF (15 g) was placed in the 2l pot of a Braun Combimax 700 food processor with 1200 ml of water. To this was slowly added Nymcel (45 g), with gentle stirring. Once the addition had been completed, the mixture was stirred for 10 minutes, allowed to stand for 15 minutes and finally stirred for 2 minutes. The mixture was then transferred into a 5 litre beaker and acetone (2.5l) added. The mixture was stirred for 15 minutes before the acetone was decanted off. More acetone (360 ml) was then added to the wet solid mass and stirred for 15 minutes before the acetone was decanted off. This last operation was repeated twice before the wet solid material was transferred in a vacuum oven to dry (for 24 hours at 60°C under 10 mm Hg). All the dry material was returned to the food processor, ground and sieved, yielding three fractions of 25% CMF coated with 75% Nymcel: Between 1mm and 2 mm in diameter: 15.5g

Between 0.5 mm and 1 mm in diameter: 7.07g

Below 0.5 mm in diameter: 31.57g

Example 5: Preparation of 85 wt % active Disintegrating Component(25% CMF coated with 75% Nymcel) + 15% Glycerol

Curly cellulose CMF (15 g) was placed in the 2l pot of the Braun Combimax 700 food processor with 1200 ml of water. To this was slowly added Nymcel (45 g), with gentle stirring. Once the addition was completed, the mixture was stirred for 10

minutes, allowed to stand for 15 minutes and finally stirred for 2 minutes. The mixture was then transferred into a 5 litre beaker and acetone (2.5l) added. The mixture was stirred for 15 minutes before the acetone was decanted off. More acetone (360 ml) was then added to the wet solid mass and stirred for 15 minutes before the acetone was decanted off. This last operation was repeated twice before the wet solid material was transferred in a vacuum oven to dry (for 24 hours at 60°C under 10 mm Hg). 52 g of dry material was returned to the food processor and ground such that all of the material produced has a diameter under 1mm, most of it being around 0.5 mm or below. 47.21 g of ground material were agglomerated with 8.33 g of glycerol and the agglomerated material was sieved such that all material has a diameter d of $0.5 \text{ mm} < d < 1 \text{ mm}$. This yields 50 g of 85% (25% CMF coated with 75% Nymcel) + 15% Glycerol.

Example 6: Preparation of 85 wt % active Disintegrating Component (50% CMF coated with 50% Nymcel) + 15% Glycerol

The preparation was in example 5 but using 30 g of Curly cellulose CMF instead of 15 g and 30 g of Nymcel instead of 45 g.

Example 7: Preparation of 85 wt % active Disintegrant Component (10% CMF coated with 90% Nymcel) + 15% Glycerol

The preparation was in example 5 but using 6 g of Curly cellulose CMF instead of 15 g and 54 g of Nymcel instead of 45 g.

Example 8: Preparation of 66 wt % active Disintegrating Component (25% CMF coated with 75% Nymcel) + 33% stearic acid

The preparation was in example 5 but using 23.6 g of melted stearic acid instead of 8.33 g of glycerol in the final agglomeration step.

Example 9: Preparation of 85 wt % active Disintegrating Component (25% CMF coated with 75% CMC MW 250 000, d.s. 0.7) + 15% Glycerol

The preparation was in example 5 but using 45 g of Carboxymethyl Cellulose (CMC) of average molar weight 250000 and average degree of substitution d.s. 0.7 instead of 45 g of Nymcel.

Example 10: Preparation of 85 wt % active Disintegrating Component (25% CMF coated with 75% CMC MW 700 000,d.s. 0.9) + 15% Glycerol

The preparation was in example 5, but using 45 g of Carboxymethyl Cellulose (CMC) of average molar weight 700000 and average degree of substitution d.s. 0.9 instead of 45 g of Nymcel.

Example 11: Preparation of 85 wt % active Disintegrating Component (25% Arbocel coated with 75% Nymcel) + 15% Glycerol

The preparation was as in example 5 but using 15 g of Arbocel instead of 15 g of Curly cellulose CMF.

The products of examples 1 to 11 were mixed, by dry mixing into a pre-formed detergent composition comprising on a parts by weight basis 2.5 pbw LAS, 2.0 pbw AS, 8 pbw AES, 1 pbw QAS, 6 pbw sodium citrate, 13 pbw zeolite, 9 pbw Na SKS-6, 12 pbw sodium percarbonate, 5 pbw TAED, 0.25 pbw chelant, 0.5 pbw HEDP, 0.45 pbw CMC, 0.31 pbw SRP, 2.87 pbw MA/AA, 0.12 pbw Brightener 15, 0.02 pbw Brightener 49, 0.96 pbw, 17.36 pbw Carbonate, 0.52 pbw Sodium Sulphate, 0.37 pbw Silicate 2,OR, 1.43 pbw PEG, 0.20 pbw suds supressor (silicone) 1.30 pbw Soap. The dry compositions were then formed into tablets by compaction.

Tabletting

The tablets of the present invention were prepared by compaction of a particulate detergent composition, according to the procedures described in European Patent Applications EP 0 598 586 A1 page 9, lines 21 to 44 and EP O 481 792 A1 page 7, lines 1 to 20.

The tablets were prepared using either an Instron™ 4469 Compaction and Tension Tester, an Instron™ Universal Testing Machine or a Lloyd™ LR50K Material Testing Machine. Tablets were pressed automatically to a given load to produce

tablets comprising different disintegrating components but with comparable fracture stress, so that disintegration performance could be assessed. All tablets produced had a diameter of 54mm. Unless otherwise stated in table 1, all tablets were made up of 50g pre-formed detergent matrix as set out above and 2.5g disintegrating component. As a measure of the resistance of the tablets to fracture, the diametral fracture stress was determined according to the equation described in EP 0 598 586 A1 page 9, lines 36 to 41. Preferred tablets of the invention have a diametral fracture stress of at least 5 kPa. Disintegrating performance results for these tablets is given in table 1 below.

Disintegration Test Protocol

A tablet is gently deposited into a 2 litre beaker containing 1 litre of cold water and 7 ice cubes (20 g each). The tablet is left there unstirred for 2 minutes after which any residual solid lumps are manually picked out and weighed.

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Table 1

Disintegrant System	Diametral Fracture Stress	% residue in beaker test after 2 minutes
Tablet of 50g of detergent matrix + 0.5g of finely ground CMF (1 wt% CMF)	36.0kPa 28kPa	>95% 83%
Tablet made of 50g of detergent matrix + 1.5g of Nymcel (3 wt% Nymcel) (Comparative example)	35kPa 25kPa	>95% >95%
Agglomerate of example 1	40kPa 35kPa 25kPa	>95% >95% 93%
Disintegrating Component of Example 4 (fraction d < 0.5 mm)	30kPa	60%
Disintegrating Component of Example 5	40kPa 25kPa	70% 20%
Disintegrating Component of Example 7	40kPa	85%
Agglomerate of example 2	25KPa	60%
Disintegrating Component of Example 8	25KPa	30%
Tablet of 50g detergent matrix + 1.5g CMC MW 250 000, d.s. 0.7	40kPa	>95%
Tablet of 50g detergent matrix + 3% CMC MW 700 000, d.s. 0.7 (Comparative example)	25kPa	>95%
Disintegrating Component of Example 9	45 kPa	70%
Disintegrating Component of Example 10	25kPa	70%
Tablet made of 50g of detergent matrix + 0.5g of Arbocel (1.0 wt% Arbocel)	35kPa 27kPa	>95% 92%
Agglomerate of Example 3	40kPa	72%
Agglomerate of Example 11	42.5kPa	60%

Example 12

The following are examples of detergent compositions according to the invention.

They may be particulate or may be compressed in a tablet press into tablets.

	A	B	C	D
Base Powder				
STPP		-	10.0	-
Zeolite A	16.0	-	-	16.0
C45AS	4.0	-	4.0	5.0
QAS I	-	1.0	-	-
MBAS 17, 2.1	2.0	4.0	-	-
C25 AE ₃ S	-	1.0	-	1.0
MA/AA	2.0	1.0	2.0	1.0
LAS	10.0	11.0	8.9	6.6
TAS	-	4.0	-	-
Silicate	-	3.0	-	3.0
CMC	1.0	1.0	0.5	1.0
Brightener 2	0.2	0.2	-	-
Soap	1.0	-	-	1.0
DTPMP	0.4	0.4	0.2	0.4
NaSKS-6	9.0	16.0	10.0	6.8
Spray On				
C45E7	-	2.5	-	-
C25E3	2.5	-	-	-
Silicone antifoam	0.3	0.3	0.3	0.3
Perfume	0.3	0.3	0.3	0.3
Disintegrating comp. of e.g. 1	2.0	1.3	3.0	2.5
QEA	-	0.5	1.0	-
Carbonate	6.0	13.0	15.0	13.0
PB4	18.0	18.0	10.0	-
PB1	4.0	4.0	-	-
NOBS	3.0	4.2	1.0	-
Photoactivated bleach	0.02	0.02	0.02	0.02
Manganese catalyst	-	-	0.5	-
Protease	1.0	1.0	1.0	1.0
Lipase	0.4	0.4	0.4	0.4
Amylase	0.25	0.30	0.15	0.3
Dry mixed sodium sulfate	3.0	3.0	5.0	3.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0	100.0
Density (g/litre)	630	670	670	670

	E	F	G	H
Base product:				
TAS	-	1.0	4.0	-
MBAS 17, 1.9	5.0	10.0	16.0	8.0
C45AS	4.0	4.0	6.0	6.0
MES	3.0	-	-	-
QAS II	0.4	-	1.0	-
TFAA	-	1.0	-	-
C25E5/C45E7/C2 5E3	-	2.0	-	1.0
LAS	-	18.0	-	-
Zeolite	9.0	5.0	-	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DTPMP	0.7	1.0	-	-
SRP I	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NACA	-	-	-	3.0
NAC OBS	2.0	1.0	0.9	3.1
Disintegrating component of example 2	4.0	6.0	3.0	2.0
Agglomerate:				
SKS-6 (I)	6.6	6.0	20.0	10.0
LAS	3.0	-	15.0	7.0
C45 AS	3.0	6.0	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100

	I	J	K
Base Powder			
MBAS 17.5, 1.8	-	-	2.0
Zeolite A	-	22.0	6.0
Sodium sulfate	1.0	5.0	-
MA/AA	3.0	3.0	3.0
MES	-	5.0	-
LAS	-	-	3.5
C45AS	3.0	4.0	7.0
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener I	0.2	0.2	0.2
Carbonate	8.0	16.0	5.0
Citric acid	3.0	2.0	1.5
Spray On			
C45E5	1.0	1.0	-
LAS/MES	8.0	5.0	5.0
Dry additives			
NaSKS-6	15.0	6.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NOBS	-	6.1	-
NAC OBS	-	-	4.5
Disintegrating component of example 5	-	-	1.0
Disintegrating component of example 6	2.5	4.6	-
Sodium sulfate	-	6.0	-
Balance (Moisture and Miscellaneous)	100	100	100

		L	M	N
Blown Powder A	Zeolite	-	-	15.0
	Sodium sulfate	0.0	5.0	0.0
	LAS	9.0	7.0	7.0
	C45AS	7.0	2.0	4.0
	QAS	-	-	1.5
	DTPMP	0.4	0.4	0.4
	CMC	0.4	0.4	0.4
	MA/AA	4.0	2.0	2.0
	Agglomerate QAS	1.0	-	-
	LAS	-	11.0	7.0
	TAS	2.0	2.0	1.0
	Silicate	2.0	-	4.0
	Zeolite A	8.0	8.0	8.0
	Carbonate	7.0	8.0	4.0
Spray On	Encapsulated Perfume	0.3	0.3	0.3
	C25E3	2.0	-	2.0
Dry additives	NaSKS-6 silicate	15.0	12.0	5.0
	QEA	1.0	0.5	0.5
	Citric/Citrate	5.0	-	2.0
	Bicarbonate	-	3.0	-
	Carbonate	8.0	15.0	7.0
	NAC OBS	6.0	-	5.0
	Manganese catalyst	-	-	0.3
	NOBS	-	2.0	-
	PB1	14.0	7.0	10.0
	Polyethylene oxide of MW 5,000,000	-	-	0.2
	Bentonite clay	-	-	10.0
	Citric acid	-	-	0.5
	Protease	1.0	1.0	1.0
	Lipase	0.4	0.4	0.4
	Amylase	0.6	0.6	0.6
	Cellulase	0.6	0.6	0.6
	Silicone antifoam	5.0	5.0	5.0
	Agglomerate of example 2	5.0	2.0	3.0
	Sodium sulfate	0.0	1.0	0.0
Balance (Moisture and Miscellaneous)		100.0	100.0	100.0
Density (g/litre)		850	850	850

	O	P	Q	R
Agglomerate				
QAS	2.0	-	2.0	-
MES	-	2.0	-	-
LAS	6.0	-	-	-
TAS	-	2.0	-	-
C45AS	6.0	4.0	2.0	-
MBAS16.5, 1.9	4.0	-	-	-
Zeolite A	15.0	6.0	-	-
Carbonate	4.0	8.0	4.0	8.0
MA/AA	4.0	2.0	-	2.0
CMC	0.5	0.5	-	0.5
DTPMP	0.4	0.4	-	0.5
Spray On				
C25E3	1.0	1.0	-	-
Perfume	0.5	0.5	0.5	0.5
Agglomerate				
NaSKS-6	7.0	13.0	20.0	9.0
LAS	5.8	9.0	15.0	9.0
Zeolite	-	0.9	-	-
C45 AS	-	3.0	-	-
Water	0.08	0.1	-	0.2
Dry Adds				
EDDS/HEDP	0.5	0.3	0.5	0.8
NaSKS 6 (I) or (II)	5.0	-	-	-
Citrate	-	1.0	-	-
Citric acid	2.0	-	2.0	4.0
NAC OBS	4.1	-	5.0	4.0
TAED	0.8	2.0	-	2.0
Percarbonate	14.0	18.0	13.0	16.0
SRP 1	0.3	0.3	-	0.3
Protease	1.4	1.4	1.0	0.5
Lipase	0.4	0.4	0.3	-
Cellulase	0.6	0.6	0.5	0.5
Amylase	0.6	0.6	-	0.3
QEA	1.0	-	1.0	1.0
Silicone antifoam	1.0	0.5	0.5	1.5
Brightener 1	0.2	0.2	-	6.2
Brightener 2	0.2	-	0.2	-

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Disintegrant component of example 7	6.0	-	2.0	3.0
Disintegrating comp. of e.g. 8	-	4.0	-	-
Density (g/litre)	850	850	800	775

Example 6

	S	T	U	V	W	X
C45AS	11.0	5.0	4.6	6.5	4.1	9.0
C25AES	1.3	1.0	-	1.3	1.0	-
LAS	10.0	3.0	12.7	10.0	5.0	9.5
C25E3/ C25E5	1.5	4.7	3.3	-	4.7	3.3
MBAS 16.5, 1.7	15.0	12.0	10.0	10.2	7.0	14.1
QAS	-	1.15	0.6	-	1.7	-
Zeolite A	5.0	16.7	-	7.0	16.7	11.2
Disintegrating component of example 2						
Citric acid	-	1.5	2.5	-	1.5	-
MA/AA	-	0.6	-	-	0.6	-
MA/AA 3	-	-	7.03	-	-	7.03
AA	2.3	-	-	2.8	-	-
EDDS	-	0.3	-	-	0.3	-
HEDP	-	0.5	-	-	0.5	-
Carbonate	6.0	12.5	14.5	6.0	12.5	14.0
SKS-6/silicate	10.58	0.8	20	10.58	4.8	20
PBI	11.0	-	14.0	-	-	4.0
NACA-OBS	-	4.7	-	-	2.7	-
PC	-	17.3	-	20.0	17.3	-
NOBS	-	-	4.0	-	-	4.0
TAED	-	2.5	-	-	3.5	2.0
Protease	0.25	0.36	0.2	0.26	0.36	0.2
Lipase	-	-	-	-	-	-
Cellulase	0.3	0.26	-	0.3	0.26	-
Amylase	-	0.36	-	-	0.36	-
Brightener	0.17	0.06	0.30	0.17	0.06	0.30
SRP1	0.4	0.2	0.5	0.4	0.2	0.5
PEG	1.6	-	0.19	1.6	-	0.19
Sulfate	5.5	6.4	3.5	5.5	6.4	3.5
CMC	-	0.5	-	-	0.5	-
MgSO ₄	-	0.13	-	-	0.13	-
Photobleach	-	0.0026	-	-	0.0026	-
Agglomerate of example 3	3.5	3.0	2.0	3.0	4.0	3.0
Silicone anti-foam	0.02	0.21	0.17	0.02	0.21	0.17
Perfume	0.42	0.55	0.25	0.42	0.55	0.25

	Y	Z	AA	AB
MBAS 16.5, 1.7	-	-	-	5.5
C45 AS	9.0	8.0	4.1	4
C45E1S	1.0	-	-	-
LAS	8.0	4.0	19.7	5.0
CI6 SAS	-	2.0	-	-
MES	-	-	-	4
C23E6.5	-	1.5	-	1.5
NaSKS-6	10.0	6.0	19.0	7.0
Zeolite A	7.8	17.0	-	20.0
AA	2.3	2.3	2.3	2.3
Carbonate	7.0	7.0	12.5	2.5
Silicate	0.6	0.6	0.6	-
Perborate/PC	11.0	2.0	-	-
Protease	0.3	0.3	0.3	0.3
Cellulase	0.3	0.3	0.3	0.3
SRP1	0.4	0.4	0.4	0.4
Brightener	0.2	0.2	0.2	0.2
PEG	1.6	1.6	1.6	1.6
Sulfate	5.5	5.5	5.5	5.5
Silicone Antifoam	0.42	0.42	0.42	0.42
Disintegrant composition of example 8	2.0	2.0	6.0	4.0
Disintegrant composition of example 4	-	2.0	-	1.0
Moisture & Minors	---Balance---			
Density (g/L)	663	663	663	663

	AC	AD	AE	AF	AG
MBAS 16.5, 1.7	14.8	16.4	12.3	8.2	4.1
C45 AS	6.0	8.0	4.3	4.0	5.0
C45E1S	2.0	-	-	1.0	-
LAS	-	-	-	3.0	5.0
C16 SAS	-	1.0	-	-	-
MES	-	5.0	-	-	-
TFAA	1.6	0	0	0	0
C24E3	4.9	4.9	4.9	4.9	4.9
Zeolite A	5.0	15	-	-	-
NaSKS-6/LAS agglomerate with ratio 3:2	21	10	30	17	20
Citrate/citric	1.0	3	3	2.0	-
MA/AA	4.8	4.8	4.8	4.8	4.8
HEDP	0.5	0.5	0.5	0.5	0.5
Carbonate	8.5	8.5	8.5	8.5	8.5
Percarbonate	20.7	20.7	20.7	20.7	20.7
TAED	4.8	4.8	-	-	4.8
NACA-OBS	-	-	5.0	6.0	2.0
Protease	0.9	0.9	0.9	0.9	0.9
Lipase	0.15	0.15	0.15	0.15	0.15
Cellulase	0.26	0.26	0.26	0.26	0.26
Amylase	0.36	0.36	0.36	0.36	0.36
SRPI	0.2	0.2	0.2	0.2	0.2
Brightener	0.2	0.2	0.2	0.2	0.2
Sulfate	2.3	2.3	2.3	2.3	2.3
QEA	1.0	1.0	-	-	-
QAS	1.0	-	-	-	1.0
Silicone Antifoam	0.4	0.4	0.4	0.4	0.4
Agglomerate of example 2	3.0	3.0	-	-	1.5
Disintegrating component of example II	-	-	3.0	3.0	2.0
Moisture & Minors	---Balance---				
Density (g/L)	850	850		850	850

	AH	AI	AJ	AK	AL
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	8.0	-	8.0	-	7.0
C25AE3S	0.5	2.0	1.0	-	-
LAS/NaSKS-6 Agglomerate with ratio 3:2	5.0	17.0	9.0	20.0	15.0
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	10.0	10.0	-	10.0
NaSKS-6 (H) (dry add)	-	-	2.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric acid	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
PC	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
Agglomerate of example 1	4.0	4.0	4.0	4.0	4.0
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Enzyme	0.3	0.3	1.0	1.0	0.2
Minors (Brightener/SRP1/ CMC/Photobleach/ MgSO ₄ / PVPVI/Suds suppressor/ PEG)	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1

Claims

1. A detergent composition or component thereof comprising cross-linked cellulose.
2. A detergent composition or component thereof according to claim 1 in which the cross-linked cellulose is fibrous, the fibres having a length to diameter ratio of at least 3:1.
3. A detergent composition according to claim 1 or claim 2 in which at least 50% of the number of cross-linked chemical bonds comprise intrafibre cross-linking.
4. A detergent composition according to any preceding claim in which the cross-linked chemical bonds in the cross-linked cellulose are produced by carboxylic acid cross-linking.
5. A detergent composition according to any preceding claim in which the cross-linked chemical bonds in the cross-linked cellulose are produced by citric acid cross-linking.
6. A detergent composition according to any preceding claim additionally comprising a water-swellaable agent.
7. A detergent composition according to claim 6 in which the cross-linked cellulose and water-swellaable agent are in an intimate mixture.
8. A detergent composition according to claim 7 in which the intimate mixture is in the form of water-swellaable agent coated onto the cross-linked cellulose.
9. A detergent composition according to any of claims 6 to 8 in which the water-swellaable agent comprises a polymer which is a polyacrylate, starch or carboxymethylcellulose or a copolymer or derivative thereof or a mixture thereof.
10. A detergent composition according to any of claims 6 to 10 in which cross-linked cellulose and water-swellaable agent are present in weight ratios of 1:20 to 2:1, preferably 1:10 to 1:1.
11. A detergent composition comprising cross-linked cellulose according to any preceding claim in the form of a detergent component particle having a particle size of from 150 to 1700 microns.
12. A method for making a detergent composition according to any of claims 6 to 10 comprising forming a granule which comprises an intimate mixture comprising cross-linked cellulose and water-swellaable agent and optional binder by mixing to form a substantially homogeneous mixture and incorporating the granule into a

detergent processing step to produce a detergent composition containing the granule.

13. A method for making a detergent composition according to any of claims 6 to 10 in which the intimate mixture is provided as a coating of a water-swellaable polymer on the cross-linked cellulose, the method comprising mixing the cross-linked cellulose and water-swellaable agent and a solvent for the water-swellaable agent such that a gel or solution of the water-swellaable polymer or slurry comprising a partially swollen water-swellaable agent incorporating the cross-linked cellulose is formed as a substantially homogeneous mixture and then removing the solvent so that a coating of the water-swellaable agent is formed on the cross-linked cellulose.
14. A detergent composition or component thereof according to any of claims 1 to 11 or prepared according to any of claims 12 or 13 in the form of a tablet.
15. A disintegrating component for use in a detergent composition comprising a wicking agent and a water-swellaable agent.
16. A disintegrating component according to claim 15 in which the water-swellaable agent comprises a water-swellaable polymer.
17. A disintegrating component according to claim 15 or claim 16 in which the wicking agent and water-swellaable agent are present in weight ratios of 1:20 to 2:1, preferably 1:10 to 1:1.
18. A disintegrating component according to any preceding claim additionally comprising a binder in an amount of from 0.5-50 wt % of the component.
19. A disintegrating component according to any preceding claim in which the wicking agent comprises fibres having a length to diameter ratio of at least 3:1.
20. A disintegrating component according to any preceding claim in which the wicking agent comprises a cross-linked cellulose.
21. A disintegrating component for use in a detergent composition according to any preceding claim in which the wicking agent has a low density at least 10% lower than the density of the composition or component thereof as a whole (based on the density of the composition or component thereof).

22. A disintegrating component according to any preceding claim in which the water-swellaable agent comprises a polymer which is a polyacrylate, starch or carboxymethylcellulose or a copolymer or derivative thereof or a mixture thereof.
23. A disintegrating component according to any preceding claim in which the water-swellaable agent and wicking agent are in an intimate mixture.
24. A disintegrating component according to claim 23 in which the intimate mixture is in the form of water-swellaable agent coated onto the wicking agent.
25. A method for making a disintegrating component according to any preceding claim comprising forming an intimate mixture comprising a wicking agent, water-swellaable agent and optional binder by mixing to form a substantially homogeneous mixture.
26. A method according to claim 25 in which the intimate mixture is provided as a coating of the water-swellaable polymer on the wicking agent, the method comprising mixing the wicking agent and water-swellaable agent and a solvent for the water-swellaable agent such that a gel or solution of the water-swellaable polymer or slurry comprising a partially swollen water-swellaable agent incorporating the wicking agent is formed as a substantially homogeneous mixture and then removing the solvent so that a coating of the water-swellaable agent is formed on the wicking agent.
27. A detergent or bleaching composition or component thereof comprising a disintegrating component according to any of claims 15 to 24 or prepared according to claim 25 or 26.
28. A detergent or bleaching composition or component thereof according to claim 27 in the form of a detergent tablet.
29. A pharmaceutical or herbicidal composition or component thereof comprising a disintegrating component according to any of claims 15 to 24 or prepared according to claim 25 or claim 26.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/18379

A. CLASSIFICATION OF SUBJECT MATTER

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/22 C11D3/37 C11D17/00 A61K9/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	GB 2 339 575 A (PROCTER & GAMBLE) 2 February 2000 (2000-02-02) claims 1-14 ---	1-14
X	WO 92 01777 A (MICRO VESICULAR SYSTEMS) 6 February 1992 (1992-02-06) claim 1 ---	1
X	EP 0 462 723 A (BP CHEM INT LTD) 27 December 1991 (1991-12-27) examples 3,4; table 2 ---	1
X	WO 98 03064 A (FMC CORP) 29 January 1998 (1998-01-29) examples 6E,6G,8A,9; tables 6,8 page 4, line 25 -page 5, line 2 page 7, line 24 - line 26 ---	1,6,7,9, 10,14

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☒ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T¹ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X¹ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- *S¹ document member of the same patent family

Date of the actual completion of the international search

10 May 2000

Date of mailing of the international search report

06. 09. 2000

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Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/US 99/18379

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 55590 A (UNILEVER PLC ;UNILEVER NV (NL)) 10 December 1998 (1998-12-10) examples 4C,4D,5E,5F ---	1,6
E	DE 299 09 404 U (THURN PRODUKTE INHABER ADOLF T) 30 September 1999 (1999-09-30) page 3, paragraph 2; claims ---	1,2
X	CA 2 217 238 A (CHEBLI CHAFIC ;CARTILIER LOUIS (CA)) 24 April 1999 (1999-04-24) page 8, line 8 - line 14; example 1; table 1 claims 1,2,8; figure 7; example 5 -----	15,29

INTERNATIONAL SEARCH REPORT

International application No
PCT/US 99/18379

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-14

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-14

A detergent composition or component thereof comprising a cross-linked cellulose; A method for making a detergent composition comprising a cross-linked cellulose and a water-swellaable agent

2. Claims: 15-29 and partially 6-14

A disintegrating component for use in a detergent composition comprising a wicking agent and a water-swellaable agent; method for making the disintegrating component; detergent or bleaching composition or component thereof comprising the disintegrating component; a pharmaceutical or herbicidal composition or component thereof comprising the disintegrating component; a detergent composition comprising cross-linked cellulose wicking agent and water-swellaable agent; method for making such a detergent

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/18379

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